COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Directed assembly of metal–organic cubes from deliberately predesigned molecular building blocks

Yunling Liu,[a] Victor Kravtsov,[b] Rosa D. Walsh,[a] Pankaj Poddar,[c] Hariharan Srikanth[c] and Mohamed Eddaoudi*[a]

[a] *Department of Chemistry, University of South Florida, 4202 E Fowler Ave (SCA400), Tampa, FL 33620, USA. E-mail: eddaoudi@cas.usf.edu*
[b] *Institute of Applied Physics of Academy of Sciences of Moldova, Academy str. 5, MD2028 Chisinau, Moldova*
[c] *Department of Physics, University of South Florida, Tampa, FL 33620, USA*

Received (in Columbia, MO, USA) 21st June 2004, Accepted 14th September 2004

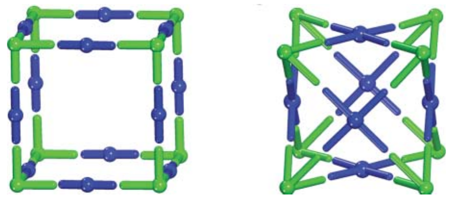
A novel anionic metal–organic cube (MOC-1), $[Ni_8(HImDC)_{12}]^{8-}$, has been synthesized by metal–ligand directed assembly of eight tri-connected Ni nodes and twelve doubly deprotonated bis(bidentate) imidazoledicarboxylic acid ligands (HImDC).

Assembly of finite supramolecular polyhedra and periodic extended networks from molecular building blocks (MBBs) offers great potential for the rational design and synthesis of functional materials and nanostructures.[1] This approach has been explored and, to some extent, has proven to be successful in metal–ligand directed assembly.[2] Metal–carboxylate based clusters, where metals are locked into their positions, have been synthesized *in situ* and successfully used as rigid directional secondary building units to design and construct stabile open metal–organic assemblies that maintain their structural integrity even upon complete removal of their guest molecules.[3] One of multiple complementary key steps suitable for the logical synthesis of crystalline metal–organic based assemblies is the ability to control the coordination number and thus geometry of inorganic and organic building units. The inorganic and organic building blocks can be judiciously predesigned to contain the required geometrical information and directional binding functionalities to facilitate the attainment of a predetermined structure.

Our approach to the design and synthesis of robust metal–organic assemblies based on single metals as vertices is to render each hetero-coordinated single metal, formed *in situ*, rigid and directional using nitrogen–oxygen chelates. The metal–nitrogen bonds will direct the topology, while the oxygen atoms will complete the coordination sphere of the metal and lock it into its position through the formation of rigid five-membered rings.

Here we report the implementation of this strategy to design and synthesize metal–organic cubes (MOCs). Blocking, *in situ*, one face of octahedrally-coordinated metals permits the formation of trigonal pyramidal building units necessary for the construction of MOCs. Two approaches can drive their assembly into supramolecular cubes, and both have previously been reported as successful:[4] (a) edge-directed assembly where the tri-connected MBBs are bridged along the edges of the cube and (b) face-directed assembly based on linking tri-connected MBBs occupying the vertices with tetra-connected MBBs, decorating the faces of the cube (Scheme 1).

Octahedrally-coordinated nickel ions prefer facial geometry, in this case *fac*-NiN_3O_3, when chelated in a five-membered fashion by N– and O– of the ligand.[5] A bis(bidentate) ligand, such as 4,5-imidazoledicarboxylic acid (H_3ImDC), permits formation of such five-membered rings (coplanar with the imidazole ring),[6] and thus coordination with nickel will lead to the construction of a metal–organic cube, where the metal–nitrogen bonds direct the topology. Indeed, reaction of H_3ImDC and $Ni(NO_3)_2{\cdot}6H_2O$ in *N*,*N′*-dimethylformamide (DMF), ethanol (EtOH) and 4,4′-trimethylenedipiperidine (TMDP) gives blue cubic crystals containing the expected metal–organic cube, MOC-1, $[Ni_8(HImDC)_{12}]^{8-}$.† The as-synthesized compound is formulated as $Ni_8(HImDC)_{12}(H_2TMDP)_4(DMF)_4(EtOH)_4(H_2O)_6$ (**1**) by elemental microanalysis and single-crystal X-ray diffraction studies.‡



Scheme 1 M_8L_{12} or $M_{12}L_8$ cube (left), M_6L_8 or M_8L_6 cube (right).

In the crystal structure of **1** (Fig. 1), each anionic cube $[Ni_8(HImDC)_{12}]^{8-}$ resides in position around the crystallographic center of symmetry and consists of eight Ni^{2+} ions occupying the vertices of the cube, and linked in a bidentate fashion by twelve HImDC *exo*-ligands. Each Ni ion is coordinated to three nitrogen and three oxygen atoms from three separate HImDC ligands, producing the facial octahedral coordination geometry, *fac*-MN_3O_3. Each ligand, stabilized by the strong intramolecular O–H···O symmetrical hydrogen bond (O···O in the range 2.50–2.55 Å), chelates two individual nickel ions to form two five-membered rings coplanar with the imidazole ring. The regularity of the cube is indicated by the fact that Ni–Ni–Ni angles lie between 88.28(1)° and 91.85(1)°, and the Ni–Ni distances along the edges are all in a narrow range 6.299–6.333 Å. The distance from the cube center to the closest non-hydrogen atom of the imidazole ring, C3, is 3.93 Å, thus the inner cavity has an estimated volume of ~ 50 Å^3 (Fig. 2). The isolated MOC-1 does not host any molecules in its cavity, and possesses an overall T_h symmetry.

Two crystallographically independent H_2TMDP cations play

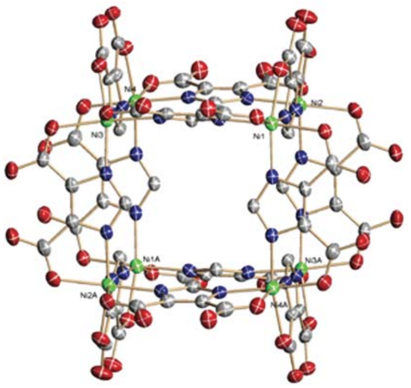


Fig. 1 Structure of the $[Ni_8(HImDC)_{12}]^{8-}$ cube showing 30% probability ellipsoids. Carbon (gray), nitrogen (blue), oxygen (red), and nickel (green) atoms shown; hydrogen atoms are omitted for clarity. Distances (û): Ni–Ni 6.299(1)–6.333(1); Ni–N 2.033(6)–2.060(5); Ni–O 2.096(5)–2.165(5). Angles (°): N–Ni–N 94.5(2)–97.8(2).

DOI: 10.1039/b409459j

distinct roles in the packing of **1** (Fig. 3). One type, illustrated in blue, bridges adjacent neighboring $[Ni_8(HImDC)_{12}]^{8-}$ cubes, along the *c*-axis, through hydrogen bond interactions (N–H···O) to form well-defined supramolecular ribbons. The second one is disordered over two positions with equal probability and joins the ribbons *via* another set of N–H···O H-bond interactions, either into a three-dimensional network, where the H_2TMDP cation (red link) bridges the ribbons concurrently along both *a* and *b* directions, or into a two-dimensional layer where the ribbons are merely linked along the *a*-axis (purple link). Taking into account the high thermal motion of the disordered cation, one can suggest that these two positions are interchangeable. The eclipsed ribbons are held together by additional hydrogen bonds through water molecules to generate one-dimensional channels along the *a*-axis where the remaining neutral guest molecules reside.

In order to evaluate the magnetic behavior of the novel octanuclear nickel cube (MOC-1), we measured the temperature dependence of its molar magnetic susceptibility (Fig. 4a). The susceptibility increases with decreasing temperatures as is typical in paramagnetic systems. However, at around 51 K, a pronounced drop in the susceptibility is observed, which can be interpreted as due to the weak antiferromagnetic ordering between nickel ion centers. The *M–H* curves at 5 K and 300 K are shown in Fig. 4b. At both temperatures the data are linear and fully reversible with no hysteresis, which is characteristic of paramagnetic behavior.

This report illustrates the potential of using N– and O– hetero-coordinated single metals, locked into their positions *via* chelation, as rigid directional building units to design and construct metal–organic assemblies where mainly the M–N bonds dictate the geometry of the inorganic building units. Expanding this approach to other metal coordination modes, MN_xO_y, is currently under investigation.

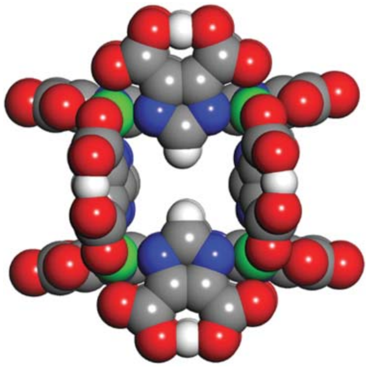


Fig. 2 Space filling model of the $[Ni_8(HImDC)_{12}]^{8-}$, MOC-1, viewed down a cube face. Carbon (gray), hydrogen (white), nitrogen (blue), oxygen (red), and nickel (green) atoms shown.

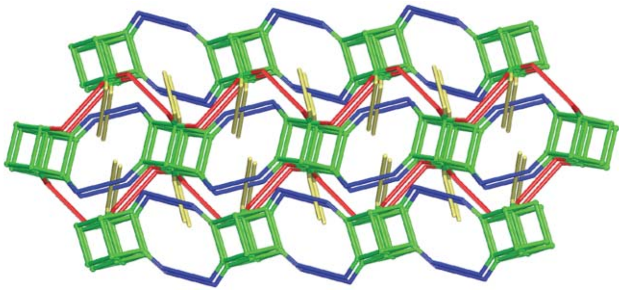


Fig. 3 An illustrative packing view of **1** along the *a*-axis, showing the cubes (green) joined together by H_2TMDP cations through N–H···O hydrogen bond interactions.

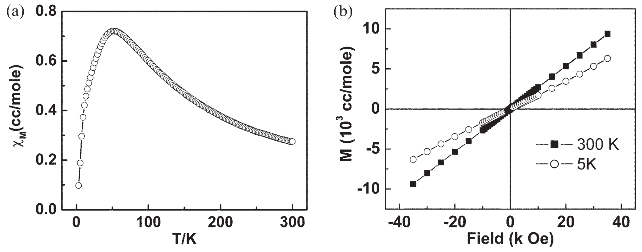


Fig. 4 (a) Magnetization *vs.* temperature for **1**. The measurements were performed at 5000 Oe magnetic field at temperatures from 5 to 300 K. (b) Magnetization *vs.* magnetic field measurements at 5 K and 300 K.

Notes and references

† *Synthesis of* **1**: 4,5-Imidazoledicarboxylic acid (0.065 mmol), $Ni(NO_3)_2\cdot6H_2O$ (0.044 mmol), DMF (1 mL), EtOH (1 mL), 4,4′-trimethylenedipiperidine (0.1 mL, 0.95 M in DMF), and HNO_3 (0.2 mL, 0.35 M in DMF) added to a 20 mL vial. Solution heated at 85 °C for 12 h, then cooled to room temperature. Blue color cubic crystals collected and air-dried (82% yield). The as-synthesized material is insoluble in water and common organic solvents. CHN elemental analysis (%) for **1**, $C_{132}H_{200}N_{36}O_{62}Ni_8$: calcd. C, 42.24; H, 5.37; N, 13.44; found C, 42.11; H, 5.23; N, 13.43. FT-IR (4000–600 cm^{-1}): 1655 (m), 1560 (w),1477 (vs), 1410 (m), 1302 (m), 1252 (m), 1110 (m), 843 (m), 783 (m), 661 (vs).

‡ *Crystal data for* **1**: $C_{132}H_{200}N_{36}O_{62}Ni_8$: $M_r = 3752.96$, monoclinic, $P2_1/c$, $a = 16.086(2)$, $b = 28.306(3)$, $c = 21.617(2)$ Å, $\beta = 102.189(2)°$, $V = 9621(2)$ Å^3, $Z = 2$, $D_c = 1.295$ g cm^{-3}, $\mu = 0.85$ mm^{-1}, 19 870 [R(int) = 0.0733] unique reflections of which 11 110 assumed as observed ($I > 2\sigma(I)$). Final $R1 = 0.0961$, $wR2 = 0.2793$ (for $I > 2\sigma(I)$). CCDC 243500. See http://www.rsc.org/suppdata/cc/b4/b409459j/ for crystallographic data in .cif or other electronic format.

1 L. R. MacGillivray and J. L. Atwood, *Nature*, 1997, **389**, 469; A. Stein, S. W. Keller and T. E. Mallouk, *Science*, 1993, **259**, 1558; C. L. Bowes and G. A. Ozin, *Adv. Mater.*, 1996, **8**, 13; A. K. Cheetham, G. Ferey and T. Loiseau, *Angew. Chem., Int. Ed.*, 1999, **38**, 3268; O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705; J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon and K. Kim, *Nature*, 2000, **404**, 982; G. R. Desiraju, *Nature*, 2001, **412**, 397.

2 B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1990, **112**, 1546; P. J. Stang and S. R. Seidel, *Acc. Chem. Res.*, 2002, **35**, 972; N. Takeda, K. Umemoto, K. Yamaguchi and M. Fujita, *Nature*, 1999, **398**, 794; S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334; M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319; D. L. Caulder and K. N. Raymond, *Acc. Chem. Res.*, 1999, **32**, 975; F. A. Cotton, C. Lin and C. A. Murillo, *Acc. Chem. Res.*, 2001, **34**, 759; K. T. Holman, A. M. Pivovar and M. D. Ward, *Science*, 2001, **294**, 1907.

3 H. Li, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276; S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148.

4 J. Faus, F. Lloret, M. Julve, J. M. Clemente-Juan, M. C. Muñoz, X. Solans and M. Font-Bardía, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1485; S. Roche, C. Haslam, H. Adams, S. L. Heath and J. A. Thomas, *Chem. Commun.*, 1998, 1681; J. L. Heinrich, P. A. Berseth and J. R. Long, *Chem. Commun.*, 1998, 1231; K. K. Klausmeyer, T. B. Rauchfuss and S. R. Wilson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1694; K. K. Klausmeyer, S. R. Wilson and T. B. Rauchfuss, *J. Am. Chem. Soc.*, 1999, **121**, 2705; A. B. F. Abrahams, S. J. Egan and R. Robson, *J. Am. Chem. Soc.*, 1999, **121**, 3535; M. C. Hong, Y. J. Zhao, W. P. Su, R. Cao, M. Fujita, Z. Y. Zhou and A. S. C. Chan, *J. Am. Chem. Soc.*, 2000, **122**, 4819; A. Zimmer, D. Kuppert, T. Weyhermüller, I. Müller and K. Hegetschweiler, *Chem. Eur. J*, 2001, **7**, 917; J. P. Lang, Q. F. Xu, Z. N. Chen and B. F. Abrahams, *J. Am. Chem. Soc.*, 2003, **125**, 12682; Z. R. Bell, L. P. Harding and M. D. Ward, *Chem. Commun.*, 2003, 2432.

5 All of the 17 crystal structures based on *tris*-chelated octahedral nickel, NiN_3O_3, deposited on the Cambridge Structure Database (CSD) are of facial geometry, *fac*-NiN_3O_3. (April 2004).

6 T. M. Rajendiran, M. L. Kirk, I. A. Setyawati, M. T. Caudle, J. W. Kampf and V. L. Pecoraro, *Chem. Commun.*, 2003, 824.